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A Bindschedler's Green-Based Arylamine: Its Polycations with High-Spin Multiplicity

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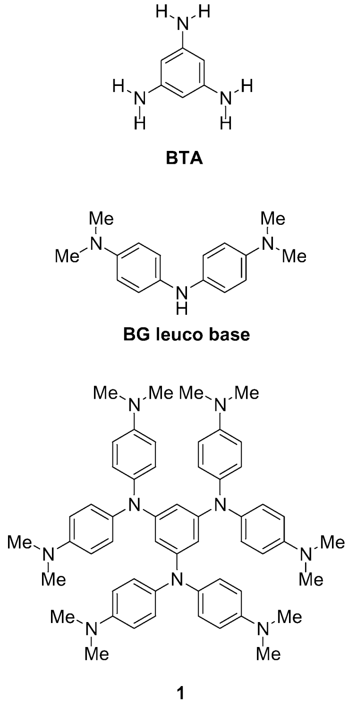
Intramolecular high-spin correlation in a series of the successively generated polycationic species of Bindschedler's green-based arylamine, *N*,*N*,*N*′,*N*′,*N*″,*N*″-hexakis[4-(dimethylamino)phenyl]-1,3,5-benzenetriamine (**1**), has been investigated by continuous wave (CW) and pulsed EPR spectroscopy. Cyclic voltammetry shows multiredox behavior of **1** that can be reversibly oxidized from monocation to hexacation. Depending on the quantity of the added oxidant, the characteristic EPR spectra are observed for polycations of **1** in frozen solution. Unequivocal determination of the spin state at each oxidation stage of **1** is given by a pulsed EPR technique, that is, electron spin transient nutation spectroscopy.

1. Introduction

Recent exhaustive investigations have revealed that arylamines are an important class of molecules for fabrication of organic-based electronic and optoelectronic devices such as photoconductors, photorefractive materials, or light-emitting devices.[1,2] In particular, they are widely used as hole-transport components in organic electroluminescent (EL) devices. Such extensive application stems from (i) the existence of their stable cationic states and (ii) their ability to form glassy amorphous phases. Among them, "star-shaped" arylamines with nominal C_3 symmetry have been examined intensively as useful hole-transport materials of organic EL devices,[2] and furthermore, their dendrimeric extension is of interest as multiredox systems or redox-gradient dendrimers.[3−5]

The above-mentioned star-shaped arylamines commonly contain 1,3,5-benzenetriamine (BTA) moiety as a core unit (Chart 1). As shown in Figure 1, BTA has triply quasi-degenerate highest occupied molecular orbitals (HOMOs), and therefore, when BTA is oxidized to dication and trication, these polycations are expected to have an open-shell electronic structure with high-spin multiplicity on the basis of the mechanism related to the Hund's rule in atomic physics.[6] In fact, BTA trication (BTA^{3+}) has been predicted to be a prototype for arylamine-based high-spin molecules.[7] Hence, its derivatives have been actively investigated so far.[8−14] However, many of the reported EPR spectra do not show clear fine-structured spectra due to a single high-spin component, probably because of (i) incomplete oxidation procedures, (ii) existence of several equilibrating radical species due to disproportionation reaction associated with the multiredox properties, and so forth. Therefore, unequivocal identification of spin multiplicities for the generated polycationic species remains to be unsettled at very low temperature.[15] Moreover, the spin multiplicity of higher oxidized species such as BTA^{4+} and BTA^{5+} is not clarified because of their instability. As shown in Figure 1, the spin preference of BTA^{4+} strongly depends on the degree of degeneracy of the frontier molecular orbitals (MOs). Therefore, at the present stage, it is not clear whether the highly charged cations such as BTA^{4+} still have the quasi-degenerate frontier MOs.

CHART 1: Molecular Structures of BTA, BG Leuco Base, and 1



The stability of the peripheral aminium moiety in the highly charged BTA-related molecule conduces to enhancement of the stability of the entire molecule. Bindschedler's green (BG) leuco base [4,4′-bis(dimethylamino)diphenylamine] is a useful and sensitive redox indicator in analytical chemistry because of the fact that BG leuco base is easily oxidized to the colored product.[16] In connection with this utility, the oxidized green

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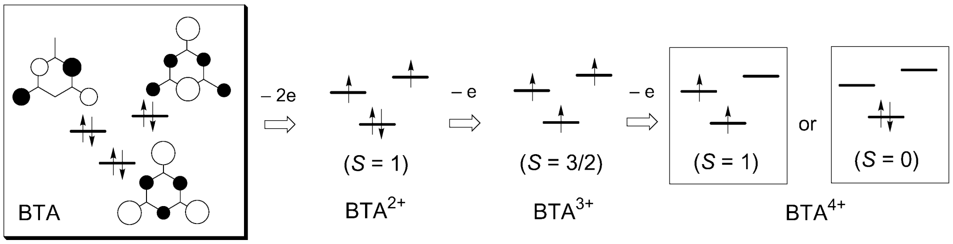

Figure 1. Triply quasi-degenerate frontier orbitals (HOMOs) of benzenetriamine (BTA) and its possible spin state for each oxidation state.

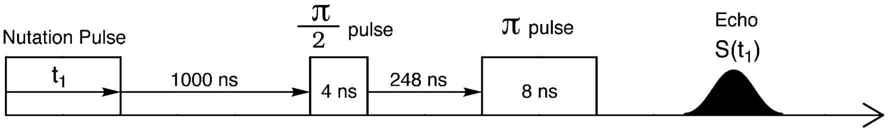

Figure 2. Pulse sequence used for the measurements of the electron spin transient nutation spectrum.

product is also recognized to be a kinetically and thermally stable cation radical (BG^+). In fact, Toman and Ocenaskova isolated BG^+ salt and, furthermore, afforded its X-ray structure.[17] Therefore, BG can be considered to be one of the effective amine moieties in the BTA-related molecules.

In this paper, we report the preparation of a BG-based arylamine [*N,N,N′,N′,N″, N″*-hexakis[4-(dimethylamino)phenyl]-1,3,5-benzenetriamine] (**1**), which can be regarded as a derivative of BTA, and the stepwise generation of its polycations. Furthermore, the spin states of the generated polycations were examined up to the hexacation on the basis of the continuous wave (CW) and pulsed EPR measurements.

2. Experimental Section

2.1. General and Materials. Commercial grade reagents were used without further purification. Solvents were purified, dried, and degassed following standard procedures. Identification of the synthesized molecule **1** was performed by the following spectroscopic measurements. ^{1}H NMR and ^{13}C NMR spectra were measured on a JEOL EX-270KS (400 MHz) spectrometer. Chemical shifts of ^{1}H and ^{13}C NMR spectra were recorded in parts per million (δ) relative to tetramethylsilane (TMS) internal standard. Low-resolution mass spectra were obtained on a JEOL JMS-700 spectrometer. Absorption spectra were recorded on a Shimadzu UV-2200 spectrophotometer. Elemental analyses were performed by Microanalytical Center, Kyoto University.

2.2 General Procedure for Synthesis of *N,N,N′,N′,N″,N″*-Hexakis[4-(dimethylamino)phenyl]-1,3,5-benzenetriamine (1). To a mixture of BG (1.0 g, 3.9 mmol), 1,3,5-tribromobenzene (0.41 g, 1.3 mmol), $Pd(dba)_2$ (35 mg, 0.060 mmol), and sodium *tert*-butoxide (0.57 g, 6.0 mmol) in Ar atmosphere were added $P(t\text{-}Bu)_3$ (10 mg, 0.050 mmol) and toluene (4 mL), and then, under a protection from light, the mixture was stirred for 20 h at room temperature under Ar. After evacuation of toluene from the resulting black solution, the residue was treated with a short column of silica gel (EtOAc as eluent). The crude product (R_f = 0.47 for EtOAc/*n*-hexane = 5/1) was recrystallized from acetone to yield **1** (0.42 g, 39%) as a white solid: mp 252 °C (dec); ^{1}H NMR (C_6D_6, 400 MHz) δ 7.34 (d, J = 9 Hz, 12H), 6.93 (s, 3H), 6.50 (d, J = 9 Hz, 12H), 2.50 (s, 36H): ^{13}C NMR (C_6D_6, 300 MHz) δ 150.72, 146.88, 139.12, 126.39, 114.20, 107.59, 40.80: MS (*m*/*z*) 838 (M^+): UV−vis (CH_3CN) λ_{max} (log ϵ) 311 (4.91): anal. calcd for $C_{54}H_{63}N_9$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.12; H, 7.54; N, 14.84.

2.3. Physical Measurements. The cyclic voltammetry (CV) measurements were recorded with 0.1 M $n\text{-}Bu_4NClO_4$ in PhCN (25 °C, scan rate 100 mV/s) using a BAS CV-50W voltammetric analyzer with a three-electrode cell using a Pt disk (2 mm^2) and a Pt wire as the working and the counter electrodes, respectively, and a Ag/0.01 M $AgNO_3$ (MeCN) as the reference electrode. EPR spectra were measured on a JEOL JES-RE-2X and JES-TE200 X-band spectrometers. Temperature was controlled by JEOL DVT2 variable-temperature unit in the range 120−180 K and by an Oxford ITC503 temperature controller combined with an ESR910 continuous flow cryostat in the range 4−100 K. The electrochemically generated EPR spectra were measured under nitrogen atmosphere using an electrochemical EPR cell, consisting of a Au helical working electrode, a Pt wire counter electrode, and a Ag wire quasi-reference electrode.[18] UV−vis spectra were recorded on a Shimadzu UV-2200 spectrometer. Pulsed EPR measurements were carried out on a Bruker ELEXES E580 X-band FT ESR spectrometer. The microwave pulse power of 10 mW provided by the microwave bridge was boosted to level of 1 kW using a traveling wave tube (TWT) amplifier. The microwave field amplitude at the sample was approximately 0.5 mT, as determined by the $\pi/2$ pulse length of 16 ns. The pulse width of the detection sequence was 4 ns and 8 ns because of optimizing the detection for the higher spin state than $S = 1$. The microwave pulse sequence used in the present study is shown in Figure 2. For the transient nutation experiment, the two-pulse electron spin−echo signal $S(t_1)$ was detected by increasing the width (t_1) of the nutation pulse. We employed appropriate phase cycles to suppress undesirable signals and artifacts which arise from an inaccurate pulse length.[19,20] The observed signal $S(t_1, B_0)$ as a function of the external magnetic field B_0 is converted into a nutation frequency domain $S(\omega_n, B_0)$ spectrum by Fourier transformation along the t_1 direction.

3. Results and Discussion

3.1. Synthesis and Redox properties of *N,N,N′,N′,N″,N″*-Hexakis[4-(dimethylamino)phenyl]-1, 3, 5-benzenetriamine (1). Thanks to recent developments in Pd(0)-based catalysis, difficulty of aromatic carbon−nitrogen bond formation reaction can be overcome and, hence, synthesis of a variety of arylamines becomes feasible. In particular, Hartwig et al. reported that this reaction occurs even at room temperature by using $Pd(dba)_2$ [dba = dibenzylideneacetone] and $P(t\text{-}Bu)_3$ in a 1:0.8 ratio.[21] To our experience, the usual copper-catalyzed reaction often fails to prepare arylamines containing *N*-methyl amino groups. Thus, we adopted the Hartwig's procedure to obtain **1**, as shown in Scheme 1.

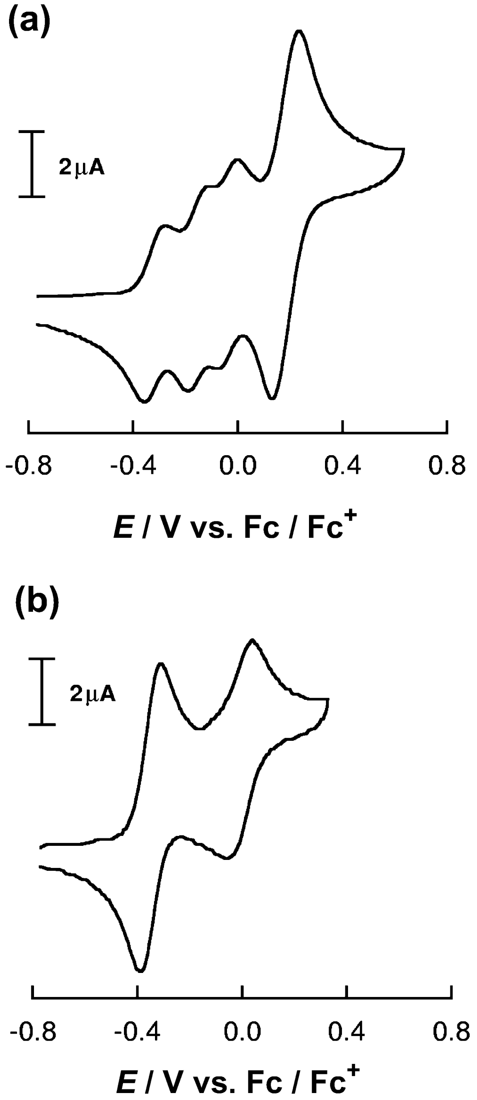

Figure 3. Cyclic voltammogram of (a) **1** and (b) BG leuco base in PhCN at 298 K, scan rate 100 mV/s.

SCHEME 1: Synthesis of 1

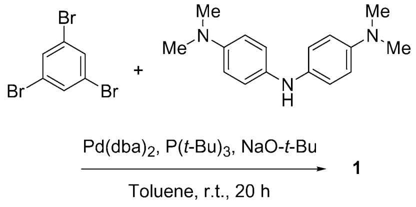

TABLE 1: Redox Potentials (in V) of 1 and BG Leuco Base[a]

compound	$E_1{}^{\circ\prime}$	$E_2{}^{\circ\prime}$	$E_3{}^{\circ\prime}$	$E_4{}^{\circ\prime}$
1	−0.32	−0.15	−0.04	+0.18[b]
BG	−0.35	+0.11		

[a] 0.1 M n-Bu_4NClO_4 in PhCN, potential versus Fc/Fc^+, Pt electrode, 298 K, scan rate 100 mV/s. [b] Quasi-three-electron oxidation.

Electrochemical oxidation of **1** by cyclic voltammetry (CV) showed four pairs of redox waves (Figure 3). The first three oxidation peaks are reversible and assigned to one-electron-transfer process with redox peak separation of ca. 70 mV. The fourth redox wave has larger peak-to-peak separation of 103 mV than the theoretical value of 57 mV,[22] and the peak current is almost 3 times as large as those of the first three oxidation peaks, suggesting that this redox wave is an overlap of three separate single-electron oxidations with a very small redox potential difference. As a whole, these results show that oxidation states +1 to +6 of **1** have lifetime longer than a few seconds in solution at 298 K. The redox potentials of **1** are summarized in Table 1 together with those of BG measured under the same conditions. As compared with the oxidation potentials of BG, it is expected that the successive three oxidation steps generate tri(cation radical) ($\mathbf{1}^{3+}$) via one-electron removal of each peripheral BG moiety, and the fourth quasi-three-electron oxidation leads to the closed-shell species ($\mathbf{1}^{6+}$).

3.2. Polycationic State of 1. Chemical oxidation of **1** (1 mM) with less than 1 molar equivalent of oxidant, tris(4-bromophenyl)aminium hexachloroantimonate (TBA•$SbCl_6$),[23] in n-butyronitrile at 203 K yielded a bluish green solution, which showed a single line EPR spectrum with no hyperfine splitting at 123 K [$\Delta B_{pp} = 0.8$ mT], indicating the generation of the mono(cation radical). When **1** in n-butyronitrile (1 mM) was treated with 2 molar equivalent of TBA•$SbCl_6$ at 203 K, the color of the solution turned blue, indicating probable generation of the corresponding di(cation radical) $\mathbf{1}^{2+}$. The EPR spectrum of $\mathbf{1}^{2+}$ at 123 K (Figure 4a) showed no detectable D splitting [$\Delta B_{pp} =$ 0.7 mT]. Apparently, the spectrum was similar to that of $\mathbf{1}^{+}$. However, direct spectral evidence for the triplet state of $\mathbf{1}^{2+}$ was obtained from the forbidden $\Delta M_S = \pm 2$ resonance at half-field (inset of Figure 4a). Three-electron oxidation of **1** at 203 K with 3 molar equivalent of TBA•$SbCl_6$ gave a blue solution of $\mathbf{1}^{3+}$, where instead of a single broad signal like those for $\mathbf{1}^{+}$ and $\mathbf{1}^{2+}$, a five-line signal characteristic of an axially symmetric quartet species was observed [$D = 3.0$ mT (0.0028 cm^{-1})] (Figure 4b). The forbidden $\Delta M_S = \pm 2$ resonance was detected at about 165 mT, whereas the $\Delta M_S = \pm 3$ resonance was not found because of the very low transition probability.[24] The observed D value is close to those of the related high-spin tri(cation radical)s with three N-centered redox sites.[25]

To check the quantitative oxidation of **1**, the absorption spectra of **1** in n-butyronitrile upon stepwise addition of 1 molar equivalent of TBA•$SbCl_6$ showed one broad band ($\lambda_{max} = 600$ nm). Moreover, the absorbance for this band increased twice and thrice with increasing the amount of added TBA•$SbCl_6$, suggesting that three BG units are oxidized in a stepwise manner. In addition, the corroborating evidence of $\mathbf{1}^{3+}$ was given by the electrochemical EPR measurements.[18] Prior to the measurements, we checked the oxidation potential by cyclic voltammetry with an electrochemical EPR cell. At a constant potential above the third oxidation potential, three electrons per molecule were removed coulometrically at 223 K, indicating the generation of $\mathbf{1}^{3+}$. After the oxidation, the sample solution was frozen at 123 K. The observed EPR spectrum was in good accordance with the spectrum shown in Figure 4b and, moreover, the forbidden $\Delta M_S = \pm 2$ resonance was also detected. This indicates that the species oxidized with 3 molar equivalent of TBA•$SbCl_6$ mainly corresponds to $\mathbf{1}^{3+}$.

Further one-electron chemical oxidation of $\mathbf{1}^{3+}$ led to loss of D splitting components [$\Delta B_{pp} = 1.0$ mT]. However, the $\Delta M_S = \pm 2$ transition could be still observed in frozen solution at 123 K, suggesting the generation of the $S = 1$ tetracationic species (Figure 4c). The shape of $\Delta M_S = \pm 1$ signal was similar to that of $\mathbf{1}^{2+}$. This suggests that the removal of two electrons from triplet $\mathbf{1}^{2+}$ does not change the spin multiplicity. The forbidden resonance faded away upon further one-electron oxidation [$\mathbf{1}^{5+}$: $\Delta B_{pp} = 2.3$ mT], and finally when six electrons were removed from **1**, the EPR spectrum revealed only traces of doublet $\mathbf{1}^{5+}$, virtually indicating the existence of a diamagnetic species $\mathbf{1}^{6+}$. For $\mathbf{1}^{5+}$, the ΔB_{pp} is rather large compared with that of $\mathbf{1}^{+}$. This probably indicates the difference of the spin density distribution between two spin-doublet species.[26]

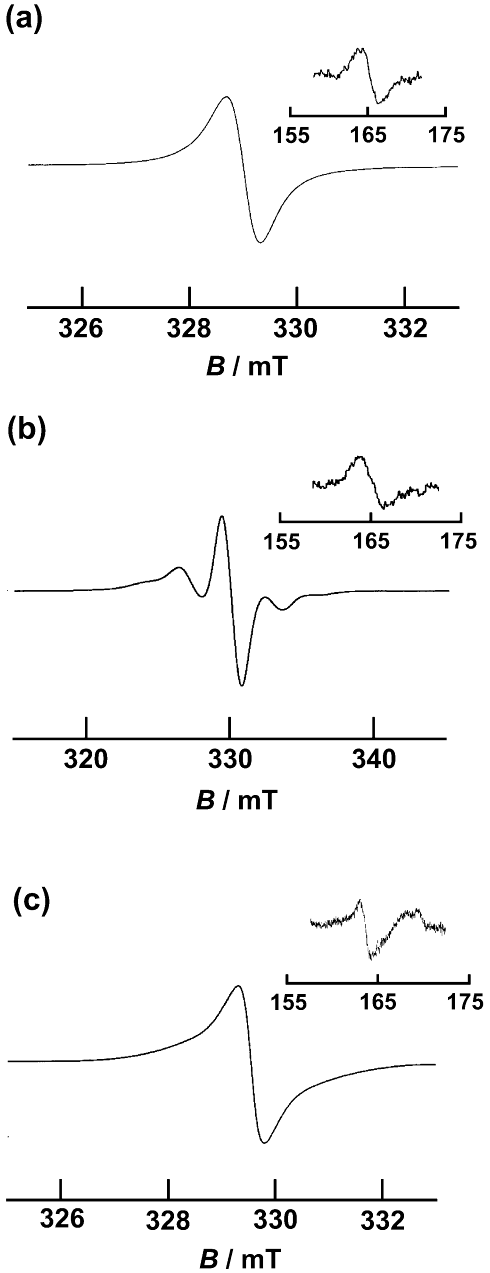

Figure 4. EPR spectra of **1** oxidized by (a) 2 molar equiv, (b) 3 molar equiv, and (c) 4 molar equiv of TBA•SbCl$_6$ in *n*-butyronitrile at 123 K. Inset: The resonance for the forbidden $\Delta M_S = \pm 2$ at 123 K.

The EPR spectra of $\mathbf{1}^{2+}$ and $\mathbf{1}^{4+}$ did not exhibit the characteristic fine structure. This is closely related to the fact that the other oxidation states such as $\mathbf{1}^{+}$ (doublet), $\mathbf{1}^{3+}$ (quartet), and $\mathbf{1}^{5+}$ (doublet) are generated because of the disproportionation of $\mathbf{1}^{2+}$ and $\mathbf{1}^{4+}$, as clearly seen later in the next section. Poly(cation radical)s of **1** are mainly produced by chemical oxidation with cation radical of tris(4-bromophenyl)amine (TBA). Judging from the high oxidation potential of TBA (~0.7 V vs Fc/Fc$^+$), it can be safely said that the added oxidant is completely consumed by oxidation of **1** in solution. However, the resulting oxidized species do not necessarily consist of a sole component owing to disproportionation originating from the multiredox properties of **1**. In the present case, the oxidation potentials for $\mathbf{1}^{3+}/\mathbf{1}^{4+}$, $\mathbf{1}^{4+}/\mathbf{1}^{5+}$, and $\mathbf{1}^{5+}/\mathbf{1}^{6+}$ redox couples are indistinguishable. Hence, as far as oxidation processes by oxidant less than four equivalent are concerned, the fraction of each polycation in solution is determined from the following three disproportionation constants, K_{c1}, K_{c2}, and K_{c3},

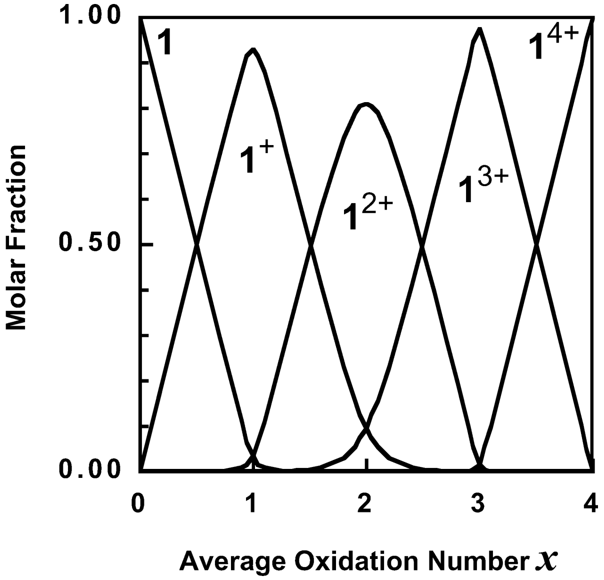

Figure 5. Molar fraction diagram for polycationic species of **1** as a function of average oxidation number (*x*).

$$K_{c1} = \frac{[\mathbf{1}^{+}]^2}{[\mathbf{1}][\mathbf{1}^{2+}]},\ K_{c2} = \frac{[\mathbf{1}^{2+}]^2}{[\mathbf{1}^{+}][\mathbf{1}^{3+}]},\ K_{c3} = \frac{[\mathbf{1}^{3+}]^2}{[\mathbf{1}^{2+}][\mathbf{1}^{4+}]} \quad (1)$$

where [**1**] and [$\mathbf{1}^{n+}$] represent the concentrations of **1** and its polycationic species $\mathbf{1}^{n+}$ (n = 1~4), respectively. From the oxidation potentials listed in Table 1, the values of K_{c1}, K_{c2}, and K_{c3} are given by the following relation,

$$\Delta E = \frac{RT}{F} \ln K_{cn}\ (n = 1{\sim}4) \quad (2)$$

where ΔE is the separation between two redox couples: $\Delta E_1 = E_2{}^{\circ\prime} - E_1{}^{\circ\prime}$, $\Delta E_2 = E_3{}^{\circ\prime} - E_2{}^{\circ\prime}$, and $\Delta E_3 = E_4{}^{\circ\prime} - E_3{}^{\circ\prime}$, and R and F are the gas and Faraday constants, respectively. Thus, the equilibrium constants are estimated to be 7.5×10, 72, and 5.3×10^3 for K_{c1}, K_{c2}, and K_{c3}, respectively. Consequently, the molar fraction of each cationic state can be obtained as a function of the average oxidation number x ($0 \le x \le 4$),

$$x = \frac{([\mathbf{1}^{+}] + 2[\mathbf{1}^{2+}] = 3[\mathbf{1}^{3+}] = 4[\mathbf{1}^{4+}])}{C_{\mathrm{tot}}} \quad (3)$$

which corresponds to the quantity of the added oxidant. Here, C_{tot} is the total concentration of neutral **1**,

$$C_{\mathrm{tot}} = [\mathbf{1}] + [\mathbf{1}^{+}] + [\mathbf{1}^{2+}] + [\mathbf{1}^{3+}] = [\mathbf{1}^{4+}] \quad (4)$$

As is evident from Figure 5, when 1−4 equivalent of oxidant are added in solution of **1**, the dominant species are expected to be $\mathbf{1}^{+}$ to $\mathbf{1}^{4+}$, respectively. However, as is the case with chemical oxidation process, it is difficult to rigorously treat with the required quantity of oxidant. Hence, undesirable oxidation states of **1** could mix in the oxidized sample, when the oxidant exceeding the integer ratio is added. In particular, the dication occupies at most 81% of the total amount of the generated cations even in the equilibrated solution treated exactly with 2 equivalent of oxidant.

Of these polycations, we confirmed that $\mathbf{1}^{2+}$, $\mathbf{1}^{3+}$, and $\mathbf{1}^{4+}$ are stable for dozens of hours in solution at ~190 K but

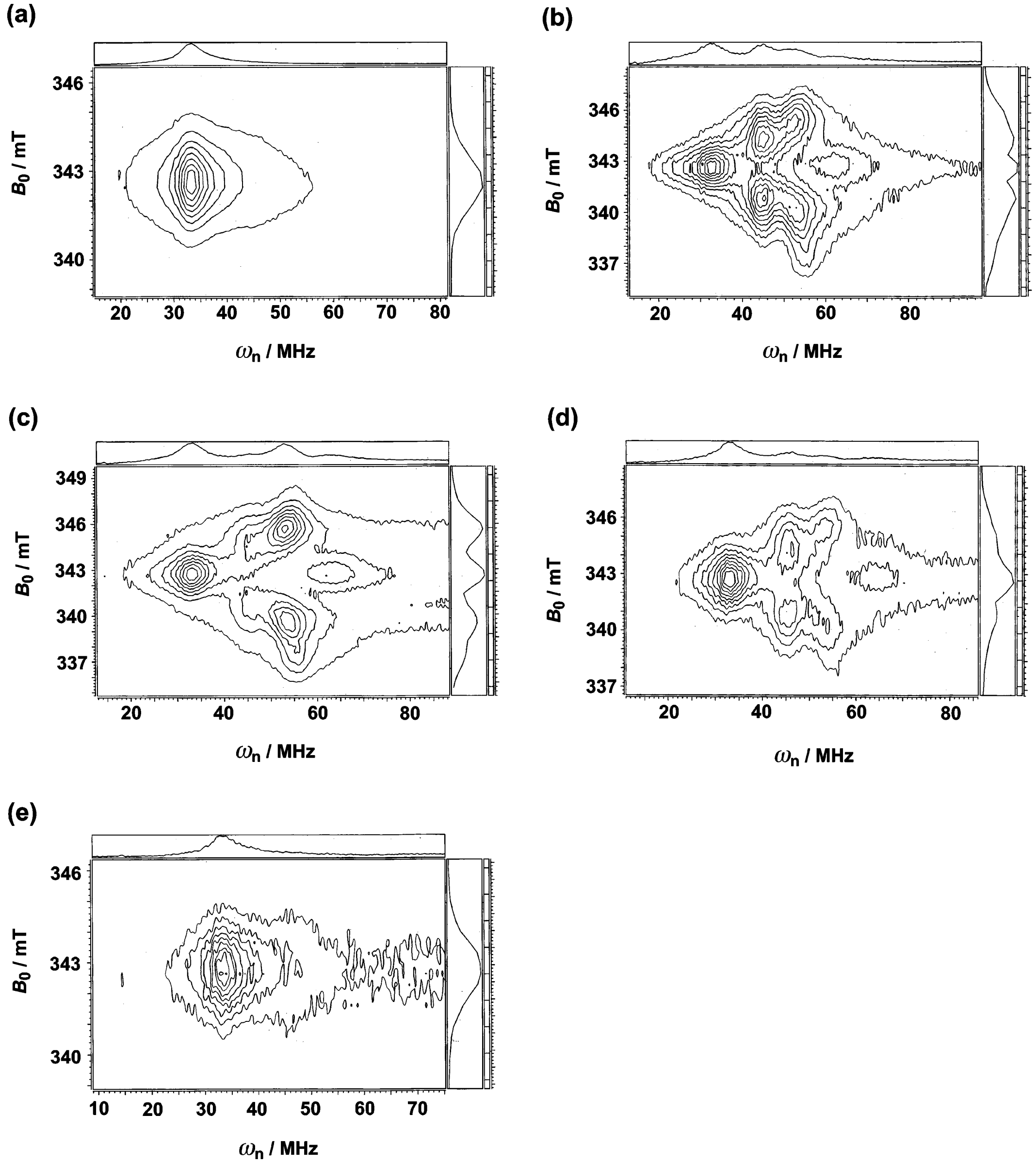

Figure 6. Field-swept electron spin transient nutation spectra of **1** oxidized by (a) 1 molar equiv, (b) 2 molar equiv, (c) 3 molar equiv, (d) 4 molar equiv, and (e) 5 molar equiv of TBA•$SbCl_6$ in *n*-butyronitrile at 5 K. ω_1 corresponds to about 30 MHz.

decompose gradually at elevated temperatures. The temperature dependence (4−100 K) of the intensity for the signal of $\Delta M_S = \pm 2$ resonance for $\mathbf{1}^{2+}$, $\mathbf{1}^{3+}$, and $\mathbf{1}^{4+}$ demonstrates a linear correlation to the reciprocal of the temperature, indicating high-spin ground state or degeneracy among the high-spin state and the other low-spin states for these polycations.

3.3. Identification of Spin Multiplicity for Each Oxidation State of 1. In the preceding section, it was found that various aspects are observed in the EPR spectra for the oxidized species of **1**, depending on the quantity of the added oxidant. However, the observed spectrum consists of a superposition of the cationic species with different spin multiplicities because of disproportionation. To identify unequivocally the spin multiplicity of the main species at each oxidation stage, we adopted the pulsed EPR method because the magnetic moments with distinct spin quantum numbers (S) precess with their specific nutation frequency (ω_n) in the presence of a microwave irradiation field (B_1) and a static magnetic field (B_0).[11,27] If the microwave irradiation field ($\omega_1 = -\gamma_e B_1$) is weak enough compared with the fine-structure parameter (ω_D in units of frequency), the nutation frequency for a transition from $|S, M_S\rangle$ to $|S, M_S{+}1\rangle$ is expressed in a good approximation, as

$$\omega_n = [S(S+1) - M_S(M_S+1)]^{1/2}\omega_1 \tag{5}$$

indicating that ω_n can be scaled with the spin quantum numbers S and M_S in a unit of the ω_n for the doublet species (ω_1).[27, 28]

In Figure 6, the relation between the echo-detected field-swept EPR spectra observed at 5 K and its transient nutation (TN) spectra is depicted in a 2-D contour representation. The projection on the magnetic field axis roughly corresponds to the usual CW-EPR spectrum, while the projection on the frequency axis corresponds to the TN spectrum. The five spectra shown in Figure 6 correspond to those when 1−5 equivalent of oxidant is added into the *n*-butyronitrile solution of **1**. As shown in Figure 6a, the nutation frequency (33.3 MHz) observed at the central field (342.5 mT) is ascribed to $|1/2, +1/2\rangle \leftrightarrow |1/2, -1/2\rangle$ transition of the doublet $\mathbf{1}^{+}$, judging from the microwave power (ω_1) dependence of the nutation frequency.

For the sample treated by 2 equivalent of oxidant, two new intense peaks at 340.8 and 344.2 mT appear and they have the same nutation frequency of 45.7 MHz, suggesting the generation of a high-spin cationic species of **1** (Figure 6b). Here, the frequency ratio (ω_n/ω_1) of 1.43 is in good agreement with the ratio of $\sqrt{2}$ expected for $|1, 0\rangle \leftrightarrow |1, \pm1\rangle$ transition of a triplet state from eq 5. As a result, the triplet species generated can be regarded as $\mathbf{1}^{2+}$. In addition, two weak peaks at 340.0 and 345.2 mT having $\omega_n = 53.3$ MHz are also observed. At the central field, a new peak having $\omega_n = 63.0$ MHz is seen in addition to that for doublet species having $\omega_n = 32.0$ MHz. The ratios between these extra nutation frequencies and 32.0 MHz for the doublet species are estimated to be 1.67 and 1.91, whose values are nearly $\sqrt{3}$ and 2, respectively. On the basis of eq 5, two peaks at 340.0 and 345.2 mT and one at the central field are assigned to $|3/2, \pm3/2\rangle \leftrightarrow |3/2, \pm1/2\rangle$ and $|3/2, 1/2\rangle \leftrightarrow |3/2, -1/2\rangle$ transitions of a quartet state, respectively. This indicates that the quartet $\mathbf{1}^{3+}$ concomitantly generates under this oxidation condition. The reason a considerable amount of $\mathbf{1}^{3+}$ is generated can be explained by the molar fraction diagram as shown in Figure 5. When a slight excess of oxidant beyond 2 equivalent is added, the ratio of $\mathbf{1}^{3+}$ increases remarkably, as is evident from this diagram.

After oxidation of **1** with 3 equivalent of oxidant, the TN spectrum clearly shows the dominance of quartet $\mathbf{1}^{3+}$ in equilibrated solution (Figure 6c). When more oxidant is added, the amount of $\mathbf{1}^{3+}$ decreases gradually. However, the doublet, triplet, and quartet species still remain after oxidation with 4 equivalent of oxidant (Figure 6d). Considering the quantity of added oxidant, the observed triplet species is regarded as $\mathbf{1}^{4+}$ and the observed doublet and quartet species are due to disproportionation reaction of $\mathbf{1}^{4+}$. In fact, judging from the oxidation potential over four-electron oxidation of **1**, the disproportionation between $\mathbf{1}^{4+}$ and $\mathbf{1}^{5+}$ is expected to become considerable. Finally, after 5 equivalent of oxidant is added, the main components in the TN spectrum consists of doublet species ($\mathbf{1}^{5+}$) and the disproportionated triplet species ($\mathbf{1}^{4+}$) (Figure 6e). Moreover, the observed decrease in intensity of doublet component is ascribed to the disproportionated diamagnetic $\mathbf{1}^{6+}$. These results are in good accordance with the CW-EPR results. Hence, the observed CW-EPR spectra without fine structures is explainable by the considerable disproportionation components. Furthermore, it was confirmed that the $\mathbf{1}^{4+}$ has triplet spin correlation, indicating that quasi-degeneracy of the frontier MOs (Figure 1) is maintained even in the highly charged state.

4. Conclusion

In conclusion, we have shown that a Bindschedler's green-based arylamine **1** gave the expected high-spin poly(cation radical)s upon two- and three-electron oxidation. Further consecutive oxidations lead to highly charged cations $\mathbf{1}^{4+}$, $\mathbf{1}^{5+}$, and $\mathbf{1}^{6+}$ with triplet, doublet, and singlet spin multiplicities, respectively. Finally, the present findings suggest that highly positive charge does not affect the quasi-degeneracy of the frontier NBMOs which determines spin preference for the polycations of **1**.

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(26) The hyperfine coupling with the nitrogen atoms causes the spectral line broadening of $\mathbf{1}^{+}$ and $\mathbf{1}^{5+}$. On the basis of the semiempirical MO calculations for a model compound of **1**, the singly occupied MO (SOMO) of $\mathbf{1}^{+}$ corresponds to one of two MOs localized on one or two of the three peripheral BG units, while the SOMO of $\mathbf{1}^{5+}$ corresponds to the MO extending over all the BG units. Hence, in $\mathbf{1}^{5+}$, there exist hyperfine interactions with much more nitrogen atoms than in $\mathbf{1}^{+}$, leading to the broader EPR spectrum of $\mathbf{1}^{5+}$.

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